ACTIVATED CHAR FROM ILLINOIS COAL FOR COMBINED SO_2/NO_x REMOVAL

Anthony A. Lizzio[1], Alex M. Chang[2] and John L.Haslbeck[2]

[1]Illinois State Geological Survey, 615 East Peabody Drive, Champaign, IL 61820
[2]NOXSO Corporation, 2414 Lytle Road, Bethel Park, PA, 15102

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INTRODUCTION

Carbon-based processes for flue gas cleanup operating in Europe [1] and Japan [2] today typically use two reactors, one to remove SO_2 and the other to remove NO_x with ammonia injection. One of the major impediments to the commercialization of this technology in the U.S. has been the cost of the activated carbon used and the fact that there is no commercial carbon on the market today that can simultaneously remove both SO_2 and NO_x from coal combustion flue gas. The NOXSO Corporation has developed a dry, post-combustion flue gas treatment system that uses a regenerable sorbent (alumina beads impregnated with 5% sodium) in a fluidized bed for combined SO_2/NO_x removal [3]. The ISGS and NOXSO are working together to develop a low cost sorbent from bituminous coal to use as an alternative sorbent in this process [4].

Numerous studies have examined NO_x removal by carbon at 300-600°C, although it is most convenient and economical to remove NO_x from flue gas at lower temperatures (100-150°C). Some studies have not used O_2 in the simulated flue gas when testing their carbons, and nearly all studies have neglected the effect of H_2O on NO_x removal. Whether activated carbon can remove significant amounts of NO_x in the presence of both H_2O and SO_2, i.e., without having to inject ammonia into the flue gas, remains to be determined. With such a carbon, only one reactor would be required to remove both SO_2 and NO_x from coal combustion flue . Today, two reactors are used because ammonia tends to react with sulfur dioxide and carbon to form ammonium sulfate, which is detrimental to activated carbon performance.

The overall objective of this study [4, 5] has been to develop a low cost activated char from bituminous coal for simultaneous removal of SO_2 and NO_x from coal combustion flue gas. Such a carbon could be used in the NOXSO process as well as in traditional fixed-bed and (less capital intensive) carbon injection processes. In this paper, we begin by examining the effect of H_2O and SO_2 on NO_x removal by activated chars shown previously in our laboratory to work well in removing SO_2 from simulated flue gas [6]. We also develop new carbons and explore the possibility of adding a catalyst to or ammonia treating activated char to enhance its combined SO_2/NO_x removal capabilities.

EXPERIMENTAL

Activated chars were prepared from an Illinois hvC bituminous coal (IBC-102) [7]. Figure 1 shows the various processing steps that were used. A 2 in. ID batch, fluidized-bed reactor (FBR) was used to pyrolyze 200 g of 48x100 mesh coal (N_2, 900°C, 0.5 h) and activate the resultant char (H_2O, 860°C, 30% conversion). The steam activated char was treated with nitric acid (10 M HNO_3, 80°C, 2 h) and thermally desorbed in N_2 or H_2 at 925°C for 1 h to desorb carbon-oxygen (C-O) complexes. A KOH activated char was prepared by mixing KOH with IBC-102 coal (2:1 KOH/coal) and pyrolyzing in the FBR (N_2, 800°C, 1 h). To prepare catalyzed chars, potassium (acetate) or sodium (carbonate) was added to IBC-102 coal by incipient wetness (IW) and pyrolyzed in N_2 (750°C, 0.5 h); the resultant char was activated in CO_2 (720°C, 2 h). In addition, K or Na was ion-exchanged (IE) onto HNO_3 treated char. Selected chars were also treated with anyhdrous NH_3 at 900°C for 2 h.

A fixed-bed adsorber (1 cm ID x 30 cm stainless steel tube) connected to a quadrupole mass spectrometer (VG Quadrupoles, Fisons Instruments) was used to obtain SO_2 and NO breakthrough curves. Typically, 6 g of char (8 cm bed height) was placed between two layers of quartz wool and heated to 120°C in flowing He (0.2 L/min). The He flow was switched to 2500 ppm SO_2, 500 ppm NO, 5% O_2 and 7% H_2O, balance He (space velocity = 2000 h^{-1}). The char sample was regenerated in situ by heating it in flowing N_2 to 525-925°C.

RESULTS AND DISCUSSION

Figure 2 presents NO breakthrough curves for several IBC-102 chars and a commercial activated carbon, Centaur carbon (Calgon Carbon). Centaur (B) removed little NO_x at 120°C, whereas the thermally desorbed IBC-102 chars (C-G) performed significantly better. The air oxidized/thermally desorbed IBC-102 char (D) was slightly better than the KOH activated char (A). Exposure of the char sample to ambient air for 48 h prior to a NO_x removal run had a detrimental effect on performance (compare C and E). Chemisorbed oxygen may poison active sites for NO adsorption/reduction. The absence of adsorbed oxygen enhances SO_2 removal by carbon [8, 9]. Carbon atoms not occupied by adsorbed oxygen atom have valence electrons more available and reactive towards SO_2. These unoccuppied or free sites control adsorption of SO_2 [9] and perhaps NO_x. Figure 2 also shows that Sample G (sample E heated to 925°C in H_2 instead of N_2) removed nearly twice as much NO_x as sample E. Treatment of char with H_2 at this temperature serves to gasify the most reactive carbons leaving behind a more stable surface, but one that still contains free sites. The more stable surface adsorbs less O_2 and H_2O at room temperature, which leads to more available sites for reaction with NO_x at 120°C.

Recent results in the literature seem to suggest that low temperature NO_x removal by activated carbon in the presence of SO_2 is not possible [10]. Figure 3 shows the effect of SO_2 and H_2O on NO_x removal by the IBC-102, HNO_3, 925°C char. The char removes 98% of the NO_x for about 1.5 h, then NO partially breaks through to about 200 ppm. For the next 15 h the [NO] increases from 200 to 300 ppm. Two NO_x removal mechanisms seem to be in effect. One where NO is simply adsorbed on the char surface and the other where the char converts NO to N_2. The catalytic mechanism

could account for incomplete breakthrough. When both SO_2 and H_2O are added at t = 17 h, large amounts of NO are desorbed. Figure 3 shows that SO_2 or H_2O (or both) displace adsorbed NO_x. This char also adsorbed the expected amount of SO_2 (111 mg SO_2/g char) even though the char was saturated with NO_x. Note that when SO_2 and H_2O were added, NO_2 was also desorbed from the char. The NO_2 desorption peak appears to coincide with the NO peak. Figure 4 shows the effect of adding H_2O and SO_2 at different times during NO_x removal. Note that the catalytic component of the breakthrough curve (200-500 ppm) no longer persists after H_2O is added. The SO_2 capacities of the IBC-102, HNO_3, 925°C chars in Figures 3 and 4 were quite similar, 111 and 99 mg SO_2/g char, respectively.

Effect of Potassium

Figure 5 shows NO breakthrough curves for char prepared from IBC-102 coal loaded with 6% K by IW. This char has a N_2 BET surface area of only 100 m^2/g compared to 500-600 m^2/g for the uncatalyzed chars shown in Figures 3 and 4. The NO breakthrough curve (no H_2O) fails to exhibit a initial period of 95-100% NO_x removal. Thermal desorption at 925°C, however, results in a 2 h period of > 98% NO removal. Thermal desorption creates free sites for NO adsorption. Figure 5 shows that this char also removes > 98% NO for about 1 h after 7% H_2O is added. A Na-loaded char prepared in a similar fashion also adsorbed NO_x with H_2O, but not to this extent.

The data shown in Figure 5 were promising. The surface area of this char could be increased through further activation, and the surface chemistry or in this case, catalyst dispersion, could be enhanced by using ion exchange instead of impregnation to load K onto the char. In an attempt to do this, steam activated IBC-102 char was treated with nitric acid, then placed in a solution of 1 M potassium acetate. The ion-exchanged char (IBC-102, HNO_3, K, IE) was then thermally desorbed at 925°C to remove chemisorbed oxygen and fix potassium atoms on the carbon surface. Figure 6 presents NO breakthrough curves with and without H_2O and SO_2 for an activated char prepared in this way (IBC-102, HNO_3, K, IE, thermally desorbed at 525°C and/or 725°C). Sample A (525°C) removed > 98% of the NO for more than 12 h without H_2O in the simulated flue gas. With H_2O and SO_2 added at t = 0 h, this char (B) performed very well in removing 98% of the NO_x for 2 h. Regeneration at 725°C (C) reduced its effectiveness, perhaps because K volatilizes at T > 700°C. When H_2O and SO_2 were again removed from the gas stream (D), NO_x removal performance improved, but not to previous levels (A).

Recent studies [11-13] have shown that K is a good catalyst for NO_x removal (without H_2O or SO_2) at relatively high temperatures (300-600°C). In TPR experiments (5°C/min), K-loaded char appeared to remove some NO_x beginning at 100°C, but it was not clear how much or whether it was even a significant amount [13]. To the best of our knowledge, the results obtained with IBC-102, HNO_3, K, IE char show for the first time that significant amounts of NO_x can be removed by activated char at 120°C in the presence of H_2O and SO_2.

Effect of Ammonia Treatment

Figure 7 shows NO breakthrough curves for steam activated IBC-102 char and the same char treated with ammonia at 900°C for 2 h. These runs, performed without H_2O in the flue gas, show that the NH_3 treatment increases the NO_x breakthrough time from 0 h to about 3 h. The ammonia treatment incorporates nitrogen into the char structure as NH_3 dissociates into N and H_2 at elevated temperaures. The H_2 can gasify the carbon if the temperature is high enough, and also deposit on the carbon surface to preserve the free sites for NO_x removal as shown in Figure 2. The surface area of the steam activated IBC-102 char increased from 465 to 580 m^2/g after the 2 h ammonia treatment. The incorporated nitrogen can have special catalytic properties. Stohr et al. [14] discussed how treatment of carbon with ammonia or hydrogen cyanide at elevated temperatures resulted in a dramatic increase in catalytic activity in oxidation reactions. The catalytic nitrogen was hypothesized to be surrounded by three carbon atoms and was situated near or at the edge of the basal plane. Most recently, Fei et al. [15] postulated that the relatively high nitrogen content of activated carbon fibers derived from shale oil was responsible for their enhanced SO_2 removal capabilities at room temperature compared to a commercial activated carbon fiber made from coal tar pitch. In our case, the NH_3 treatment has apparently increased the catalytic activity of steam activated IBC-102 char for reduction of NO to N_2 and O_2. Without the NH_3 treatment, the steam activated IBC-102 char has no activity for NO_x reduction (Figure 7).

Figure 8 show the effect of H_2O on NO_x removal by the NH_3 treated, H_2O activated IBC-102 char. Water in the flue gas inhibits NO_x removal by IBC-102 char, but it is important to note that even in the presence of H_2O, the NH_3 treated char removes 90% of the NO_x for about 1 h, which means that the catalytic properties of incorporated nitrogen are retained even in the presence of H_2O. Figure 9 shows the effect of thermal desorbing the NH_3 treated, H_2O activated IBC-102 char at 925°C for 1 h prior to a NO_x removal experiment (with no H_2O in the flue gas). There is no appreciable difference in these two NO breakthrough curves indicating that the NH_3 treatment at 900°C for 2 h essentially acts as a thermal desorption treatment in N_2 at 925°C for 1h with respect to its effect on free site concentration.

Figure 10 shows NO breakthrough curves for the NH_3 treated, H_2O activated char and the NH_3 treated, HNO_3 treated, H_2O activated char. HNO_3 treatment of the char following H_2O activation, but prior to NH_3 treatment, increases the breakthrough time from about 4 h to 10 h (without H_2O in the flue gas), a significant improvement in NO_x removal performance. Ammonia will tend to react more vigorously with the free sites generated by the nitric acid treatment than with those of the steam activated char. Nitric acid treatment of steam activated char and subsequent desorption of carbon-oxygen complexes has been shown to increase the number of carbon free sites for SO_2 adsorption [6, 9]. The generation of free sites also seems to enhance NO_x removal by activated char. Figures 3 and 4 show that SO_2 and NO_x compete for similar adsorption sites since NO_x is desorbed from the char when SO_2 is first introduced into the flue gas. Figure 10 also shows the effect of H_2O in the flue gas on NO_x removal by the NH_3 treated, HNO_3 treated, H_2O activated IBC-102 char. The NO breakthrough time is reduced by about one half, but this char still shows considerable catalytic activity. The combination of free sites and incorporated nitrogen atoms generated from the HNO_3 and NH_3 ammonia treatments, respectively, has resulted in the best performing char to date, i.e., greater than 90% NO_x removal for 4 h in

the presence of H_2O. This performance is twice as good as our previous best char (see sample B, the ion exchanged K loaded IBC-102 char, in Figure 5). A way to lower the cost of making this char would be to air oxidize (instead of HNO_3) the H_2O activated char and then react it with ammonia. The goal would be to achieve comparable SO_2/NO_x removal performance with air oxidation as was achieved with the HNO_3 treatment. The ion exchange of potassium onto this char under pH controlled conditions (pH = 9-11) could further enhance its combined SO_2/NO_x removal capabilities.

Figure 11 presents SO_2 adsorption profiles for the Centaur carbon; H_2O activated IBC-102 char; HNO_3 treated, H_2O activated char; and KOH activated char, and for these same chars treated with NH_3 at 900°C for 2 h. Three of the six IBC-102 chars outperform the commercial carbon. Ammonia treatment increases by up to 50% the SO_2 capacity (at 6 h) of these chars, which is quite remarkable. We postulate that the incorporation of nitrogen into the char and possibly the deposition of hydrogen on the char surface contributes to this dramatic increase in SO_2 adsorption capacity. The N_2 BET surface areas of the H_2O activated char and HNO_3 treated, H_2O activated char increased from 465 and 827 m^2/g to 580 and 860 m^2/g, respectively. The surface area of the NH_3 treated, KOH activated char remained unchanged at 1100 m^2/g. The NH_3 treated, HNO_3 treated, H_2O activated char had the highest SO_2 capacity (520 mg SO_2/g at 6 h) of any Illinois coal char or commercial activated carbon tested to date. This char performed well in removing NO_x in the presence of H_2O and shows tremendous potential in removing SO_2 from simulated flue gas. It is the leading candidate for use in the NOXSO process.

Integration of Activated Char into NOXSO Process

Several options are being considered for integrating ISGS activated char into the NOXSO process. One process configuration involves using activated char in a two stage system, each stage being a fluidized- or fixed-bed adsorber. The first bed could contain activated char (e.g., H_2O activated IBC-102 char) that removes greater than 98% of the SO_2 from the flue gas, but little NO_x. The second bed could contain activated char (e.g., H_2O activated, HNO_3 or air oxidized, K-catalyzed IBC-102 char) that removes greater than 90% of the NO_x from essentially SO_2-free flue gas that contains 5-12% H_2O. This char could achieve relatively high NO_x removal rates without the use of additional reagents such as ammonia. Another and probably the best scenario is to use one char and one reactor to remove both SO_2 and NO_x from the flue gas. This char could be the NH_3 treated, oxidized (either by air or nitric acid) IBC-102 char shown to remove large amounts of NO, and SO_2 from simulated flue gas (Figures 10 and 11). Another place to use activated char in the NOXSO process would be in the reheater recycle stream. If NO_x could be removed at this point in the process it would increase the overall operating efficiency of the power plant that uses the NOXSO process to clean flue gas. Instead of sending NO_x laden flue gas back to the boiler where excess NO_x is converted to N_2, a bed of activated char could be used to remove NO_x from this waste stream. The power plant could then operate independently of the NOXSO process, which is more favorable. Based on the results obtained in this study, addition of activated char to these locations in the NOXSO process (in or downstream of the fluidized-bed adsorber and/or in the reheater recycle stream) could improve the overall efficiency and lower operating costs of the NOXSO process.

CONCLUSIONS

Activated chars were prepared from Illinois coal and combined SO_2/NO_x removal experiments performed to examine the competitive effects of H_2O and SO_2 on low temperature NO_x removal. The SO_2 capacity of the char was not affected to any appreciable extent by NO in the flue gas. Both H_2O and SO_2 appeared to inhibit NO adsorption by activated char. One ion exchanged K-catalyzed char showed exceptional promise since it adsorbed significant amounts of NO even with H_2O in the gas stream. Nitric acid and/or ammonia treatment of steam activated IBC-102 char also enhanced its NO_x removal capabilities. The combination of free sites and incorporated nitrogen atoms generated from the HNO_3 and NH_3 ammonia treatments, respectively, resulted in a char that removed greater than 90% NO_x removal for 4 h in the presence of H_2O. Moreover, the NH_3 treatment of IBC-102 char increased its SO_2 adsorption capacity by up to 50%. The NOXSO process could incorporate activated char in one or more locations in their process or it may be that an entirely new process is designed based on the unique SO_2/NO_x removal capabilities of activated char.

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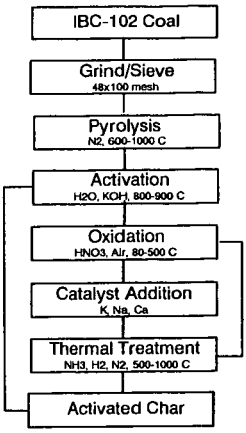

Figure 1. Production of activated char from Illinois coal.

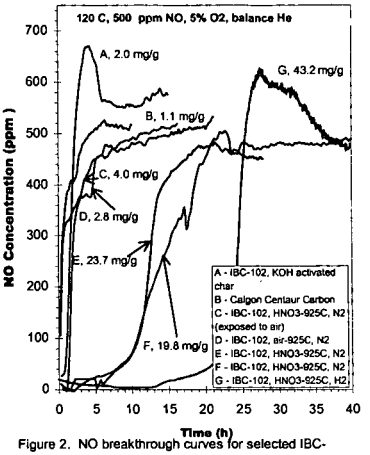

Figure 2. NO breakthrough curves for selected IBC-102 chars and a commercial activated carbon.

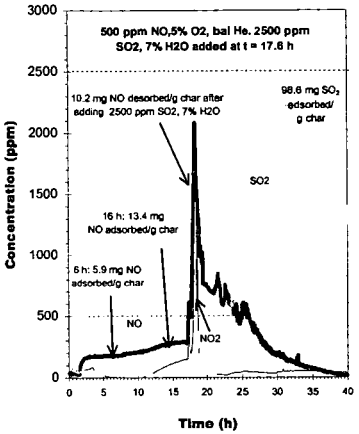

Figure 3. Effect of adding SO2 and H2O at the same time on NOX removal by IBC-102, HNO3, 925 C char.

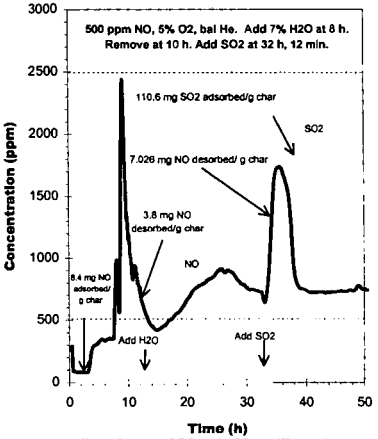

Figure 4. Effect of adding SO2 and H2O at different times in NOX removal by IBC-102, HNO3, 925 C char.

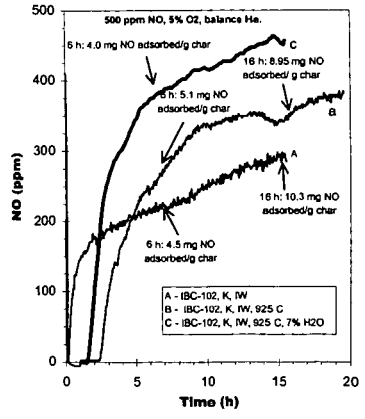

Figure 5. Effect of thermal desorption treatment (925 C) and H2O on NOx removal by IBC-102, K, IW char.

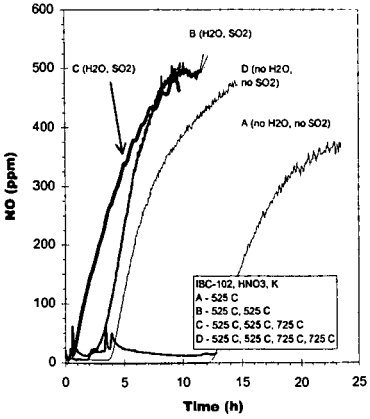

Figure 6. Effect of thermal desorption temperature and H2O/SO2 on NOX removal by IBC-102, HNO3, K, IE char.

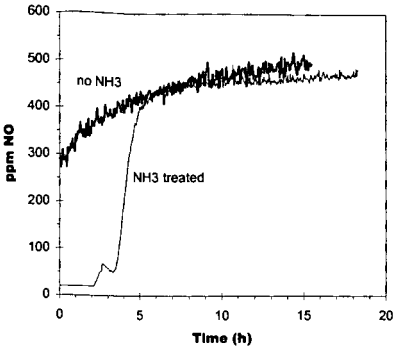

Figure 7. Effect of NH3 treatment on NOX removal by steam activated IBC-102 char.

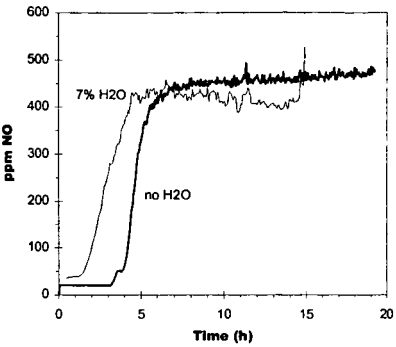

Figure 8. Effect of H2O on NOX removal by NH3 treated, steam activated IBC-102 char.

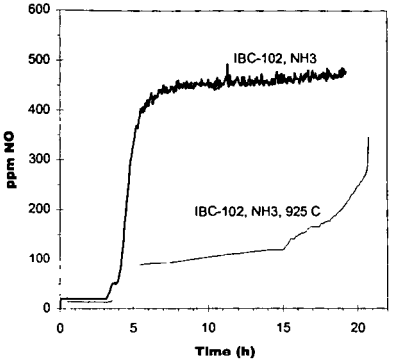

Figure 9. Effect of thermal desorption treatment at 925 C on NOX removal by NH3 treated, steam activated IBC-102 char.

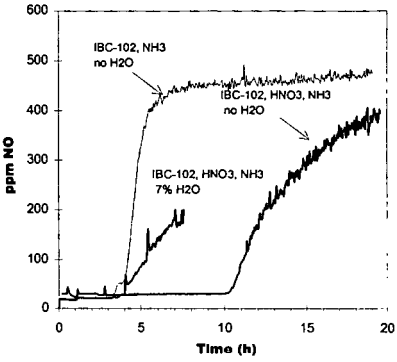

Figure 10. Effect of HNO3 treatment on NOX removal by NH3 treated, steam activated IBC-102 char.

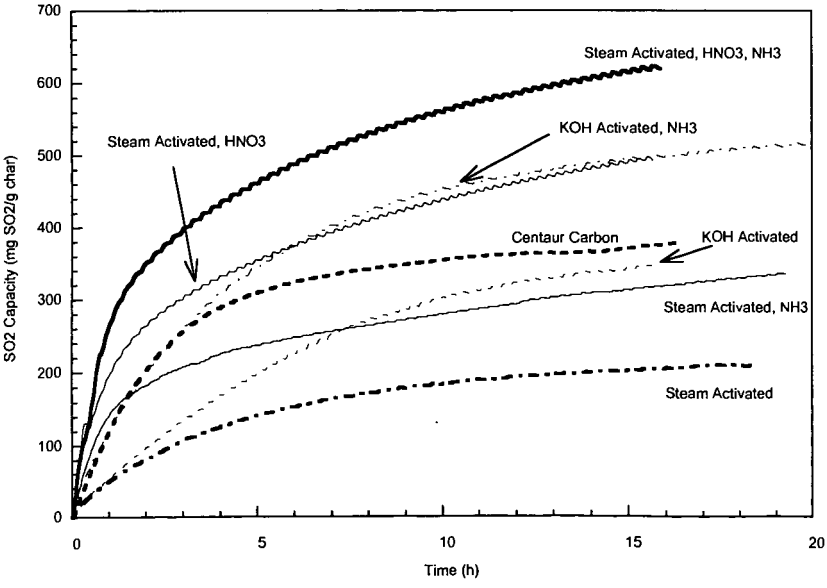

Figure 11. Effect of NH3 treatment on SO2 adsorption capacity of selected IBC-102 chars.